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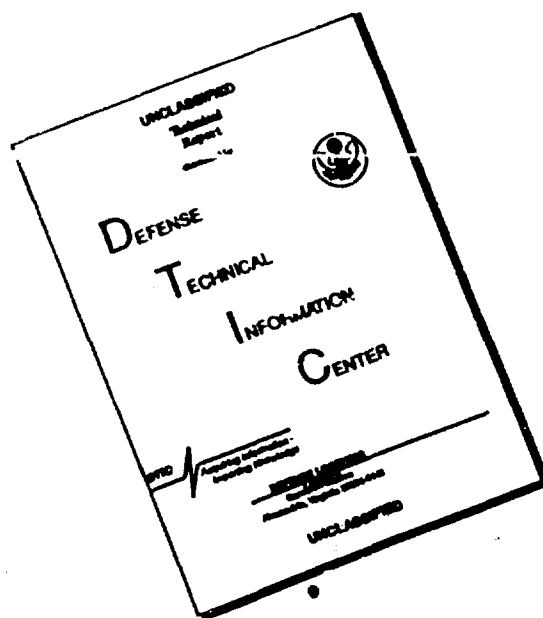
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13. ABSTRACT Tetrazene complexes and nitrene compounds derived therefrom were prepared. Attempts to use these compounds as precursors to metal nitride species failed. Metal acetylide complexes were prepared and examined by X-ray crystallography. Electrochemical procedures to deposit aluminum nitride films were explored using nonaqueous solvents. The reaction of several organometallics with azide ion was studied. The disproportionation reactions between 17-electron chromium triad radicals and various nucleophiles were characterized by infrared spectroscopy. The formation of reversible adducts from the reaction between trivalent phosphorus donor ligands and unsaturated organic carbonyl compounds was observed.			
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Final Report: Amide and Tetrazene Complexes of Transition and Main Group Elements as Precursors for the Low Temperature Synthesis of Elemental Nitrides

Grant No.: AFOSR-89-0408

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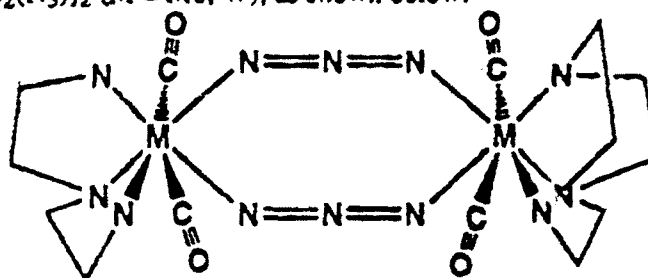
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Several tetrazene complexes, or nitrene compounds derived therefrom are described in publications 1,2,5, and 7. The body of work, summarized in publication 7 describes the utility of metal unsaturated nitrogen compounds as precursors for reactive intermediates, such as metal nitrenes. This includes several examples of insertion chemistry into unactivated C-H bonds. Attempts to use these compounds as precursors to metal nitride species failed. Thermolysis of the compounds generally results in ill-defined solid state products.

In related work to prepare metal carbides, several acetylide complexes, described in publications 3 and 6 were synthesized, as well as the cluster compound $\text{Co}_3(\text{CO})_9\text{-C}\equiv\text{C-Co}_3(\text{CO})_9$. We had hoped the latter compound might offer a low temperature route to diamond films by thermolysis under CO and the elimination of $\text{Co}_2(\text{CO})_9$. Thermolysis of these compounds failed to yield well-defined solid state products. The $\text{C}\equiv\text{C}$ π -bonds in the metal acetylide compounds were examined by X-ray crystallography. The evidence suggests there is little delocalization onto the metals and that these orbitals may lie higher than the d-orbitals, because of the significant partial negative charge on carbon.

Electrochemical procedures to deposit aluminum nitride films, were explored using nonaqueous solvents, CH_2Cl_2 and tetrabutylammonium azide electrolyte. We also examined the

reaction of several organometallics with azide ion. This could promote the formation of energetic metal azido complexes that serve as precursors to the respective nitrides. Reference 8 describes some work on a labile Cu(I) olefin complex, which was used to explore reactivity with several nitrogen nucleophiles. Furthermore there is fundamental interest in the reaction between charged radical cations and anionic nucleophiles. The disproportionation reactions between 17-electron chromium triad radicals $\text{LM}(\text{CO})_3^{\cdot}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{L} = 1,4,7\text{-tribenzyl-1,4,7-triazacyclononane}$) and $[\text{Bu}_4\text{N}]\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{N}_3, \text{SCN}, \text{SPh}$) were characterized by infrared spectroscopy. The majority of the reactions yield $\text{LM}(\text{CO})_3$ and seven-coordinate $\text{LM}(\text{CO})_3\text{X}^+$ ($\text{M} = \text{Mo}, \text{X} = \text{Cl}, \text{Br}, \text{SCN}$; $\text{M} = \text{W}, \text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$), while the reactions with N_3^- produce $\text{LM}(\text{CO})_3$ and a species assigned to $[\text{LM}(\text{CO})_2(\text{N}_3)]_2$ ($\text{M} = \text{Mo}, \text{W}$), as shown below.



$\text{M} = \text{Mo and W}$

The Cr^{II} products may undergo further oxidation to Cr^{III} in the solution. The disproportionation reactions proceed by a process second order in the metal radical and zero order in the entering nucleophile for $\text{M} = \text{Mo}$ and W . The second order rate constants (k_2) are as follows: N_3^- ($549 \text{ M}^{-1}\text{s}^{-1}$) $>$ Br^- ($26. \text{M}^{-1}\text{s}^{-1}$) $>$ Cl^- ($18. \text{M}^{-1}\text{s}^{-1}$) $>$ SCN^- ($7.1 \text{ M}^{-1}\text{s}^{-1}$) for $\text{M} = \text{Mo}$. The k_2 measured with different metal radicals are as follows: Mo ($26. \text{M}^{-1}\text{s}^{-1}$) $>$ W ($2.5 \text{ M}^{-1}\text{s}^{-1}$) for $\text{X} = \text{Br}$; Mo ($18. \text{M}^{-1}\text{s}^{-1}$) $>$ W ($3.5 \text{ M}^{-1}\text{s}^{-1}$) for $\text{X} = \text{Cl}$. Compared with the CO substitution reaction rates of 18-electron $\text{M}(\text{CO})_6$ species ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), this study shows a greatly reduced periodic effect on the reactivity of 17-electron organometallic radicals. A full paper on this research is in preparation.

In addition to the planned studies, reference 4 describes the chance observation of reversible adducts that form from the reaction between trivalent phosphorus donor ligands and unsaturated organic carbonyl compounds. This occurred in some synthetic chemistry with molybdenum.